REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
17-10-2007	Journal Article	

4. TITLE AND SUBTITLE

Facile Synthesis of Hydrophobic Fluoroalkyl Functionalized Silsesquioxane Nanostructures (Postprint)

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Scott T. Iacono & Dennis W. Smith (Clemson University); Ashwani Vij, Wade Grabow, & Joseph M. Mabry (AFRL/RZSM)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

23030521

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

AFRL/RZSM
9 Antares Road
Edwards AFB CA 93524-7401

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RZ-ED-JA-2007-478

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

AFRL-RZ-ED-JA-2007-478

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #08372A)

13. SUPPLEMENTARY NOTES

Printed in the journal *Chemical Communications*, 4992-4994, ©The Royal Society of Chemistry 2007.

14. ABSTRACT

New fluorinated polyhedral oligomeric silsesquioxane (F-POSS) structures possessing a high degree of hydrophobicity have been prepared *via* facile corner-capping methodology.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Dr. Joseph M. Mabry
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
Unclassified	Unclassified	Unclassified	SAR	4	N/A

Facile synthesis of hydrophobic fluoroalkyl functionalized silsesquioxane nanostructures†

Scott T. Iacono,[a] Ashwani Vij,[b] Wade Grabow,[b] Dennis W. Smith, Jr.[a] and Joseph M. Mabry*[b]

Received (in Cambridge, UK) 23rd August 2007, Accepted 27th September 2007
First published as an Advance Article on the web 8th October 2007
DOI: 10.1039/b712976a

New fluorinated polyhedral oligomeric silsesquioxane (F-POSS) structures possessing a high degree of hydrophobicity have been prepared *via* a facile corner-capping methodology.

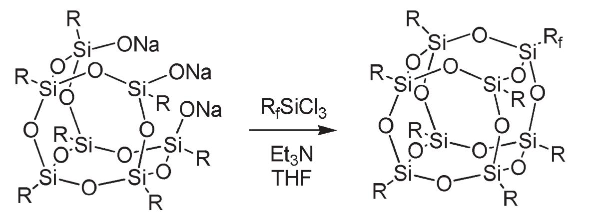
Polyhedral oligomeric silsesquioxane (POSS) compounds, comprised of a functionalized silicon–oxygen core framework, have received much interest as robust nanometer-sized building blocks for the development of high performance materials. Notable applications include surface-modified supports,[1] semiconducting materials,[2] atomic oxygen-resistant coatings[3] and high use-temperature composites.[4] A plethora of POSS compounds with the general formula $(RSiO_{1.5})_8$ can be prepared that possess a rigid, cubic core through either the acid- or base-catalyzed condensation of functionalized organosilane precursors (*e.g.*, $RSiCl_3$ or $RSi(OMe)_3$).[5] Derivatized POSS compounds can be incorporated into polymers, producing blended composites[6] and copolymers.[7] Furthermore, incompletely condensed cages have also been used as models to study heterogeneous catalyst supports.[8] Collectively, these hybrid organic–inorganic systems show an improvement in polymer properties, such as glass transition temperature, mechanical toughness, chemical resistance, ease of processing and fire resistance.

Attempts to fabricate low energy surfaces by mimicking biological organisms to produce ultrahydrophobic materials continues to gain interest.[9] Of particular interest, many plant species, including the lotus leaf, exhibit a peculiar self-cleaning mechanism as the result of micron-sized nodes decorated on the surface of the leaf.[10] Coined the "lotus effect," the intrinsic non-wetting mechanism induces water beading, and water is naturally repelled from the surface, removing any foreign debris.[11] In addition, insect species such as the Water Strider possess oriented, spindled microsetae that induce a non-wetting effect, allowing this class of spider to walk on the surface of water.[12] There are many reported approaches that successfully produce artificial, biologically replicating, non-wetting surfaces. These methods include self-assembly[13] and chemical deposition[14] of low surface energy molecules, fabrication of micron-sized ordered arrays by lithography,[15] and etching of a surface to generate nanometer- and micron-sized roughness.[16] However, there remains a need to prepare scalable low surface energy materials, since these approaches produce materials that often require aggressive chemical and/or thermal treatments, employ arduous patterning methods, produce inhomogeneous layered surfaces or generate poorly adhering coatings.

Herein, we present a new class of low surface energy POSS compounds that possess a shell of fluoroalkyl appendages encompassing the nanometer-sized POSS core. The products were prepared from commercially available materials and are amenable to scale-up to 100 g quantities. By utilizing the ability to functionalize POSS templates, the formulation of such fluorine-functionalized silsesquioxanes demonstrates a high degree of water repellency and exhibits a non-wetting behavior towards hydrocarbons. We introduce here these thermally robust POSS materials as low surface energy compatibilizers for solvent, melt or mechanical blending into polymer systems. Using these fluorinated POSS (F-POSS) compounds as modifiers for polymer blending could potentially yield water- and oil-repellant nanocomposites.

F-POSS compounds **2–7** were prepared by the condensation "corner-capping" of the hepta(3,3,3-trifluoropropyl)tricycloheptasiloxane trisodium silanolate (**1**) with fluoroalkyltrichlorosilanes in the presence of triethylamine (Scheme 1). Preparation of corner-capped POSS products has been shown to be of general utility, as demonstrated in the seminal reports by Feher *et al.*[17]

Corner capping with commercially available functionalized fluoroalkyltrichlorosilanes afforded diverse architectures, such as linear fluoroalkyl chains **2–5**, branched structure **6** and branched ether **7**. The preparation of **2** has been reported elsewhere by the base-catalyzed condensation of (3,3,3-trifluoropropyl)trichlorosilane, albeit in poor yield, requiring an extended reaction time for



1 R = $CH_2CH_2CF_3$

2 R_f = $CH_2CH_2CF_3$
3 $CH_2CH_2(CF_2)_5CF_3$
4 $CH_2CH_2(CF_2)_7CF_3$
5 $CH_2CH_2(CF_2)_9CF_3$
6 $CH_2CH_2CH(CF_3)_2$
7 $CH_2CH_2CH_2OCF(CF_3)_2$
8 CH_3
9 $CH_2CH_2C_6H_5$

Scheme 1 Preparation of fluoroalkyl$_8$T$_8$ corner-capped POSS materials *via* condensation with a trisodium silanolate, **1**.

[a]*Department of Chemistry and Center for Optical Materials Science and Engineering Technologies (COMSET), Advanced Materials Research Laboratory, Clemson University, Clemson, SC 29634, USA*
[b]*Air Force Research Laboratory, Propulsion Directorate, 10 East Saturn Boulevard, Edwards Air Force Base, CA 93524, USA. E-mail: joseph.mabry@edwards.af.mil*

† Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization of all new compounds (^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR). See DOI: 10.1039/b712976a

conversion, and leading to a mixture of octahedral (T_8) and decahedral (T_{10}) structures.[18] In comparison, this corner capping methodology offers improved yields (73–83%) of functionalized compounds **2–7**, with the exclusive formation of the desired T_8 cages. This corner-capping methodology can be easily extended to introduce a POSS with non-fluorinated alkyl **8** and aryl **9** moieties into a predominantly fluorinated environment; this is useful for generating materials with hybrid properties. In addition to the full characterization of **2–9** by employing multinuclear NMR (^{1}H, ^{13}C, ^{19}F and ^{29}Si),† X-ray structures of **2** and **8** were resolved, as shown in Fig. 1 and Fig. 2, respectively.[19] Furthermore, an interesting structure–property relationship was observed for compounds **2–5**. Melting points were depressed as fluoroalkyl chain lengths were increased from compound **2** (234–237 °C) to **3–5** (88–107 °C). The fact that attempts to grow crystals of **3–5** were difficult may help explain the observation of lower melting points due to weak crystal lattice energies. The decrease in melting points is valued for compatibility in the low temperature melt processing of these F-POSS compounds for the preparation of polymer blended nanocomposites.

The crystal structure of **2** could only be obtained as a THF solvate. In the absence of THF, the crystals rapidly turned amorphous, indicating that this solvent is necessary for lattice stabilization. The symmetric unit contains two silicon atoms, Si(1) and Si(2), which are interconnected *via* oxygen atom O(1). The fluoropropyl chain (R = $CH_2CH_2CF_3$) bonded to Si(1) showed perfect ordering, while the other fluoropropyl chain bonded to Si(2) showed two disordered positions. The POSS cage is completed by symmetry generated Si(1), O(2), and O(3) atoms along the four-fold inversion axis. The crystal packing of **2** showed an interesting Si···F interaction (see ESI†). Each of the four symmetry-generated chains forms a dimeric contact with the neighbouring POSS molecule *via* an intermolecular Si(1)···F(3) distance of 3.48 Å. The crystal structure of **8** was also elucidated to prove the diversity of the corner-capping process; its structure is

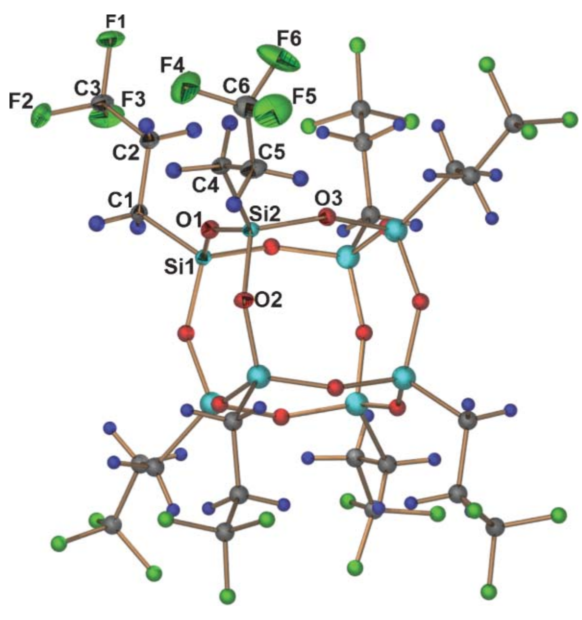


Fig. 1 ORTEP representation of **2** at 100 K showing the asymmetric atoms with displacement ellipsoids shown at 40% probability. All symmetry-generated atoms are shown as ball-and-stick models.

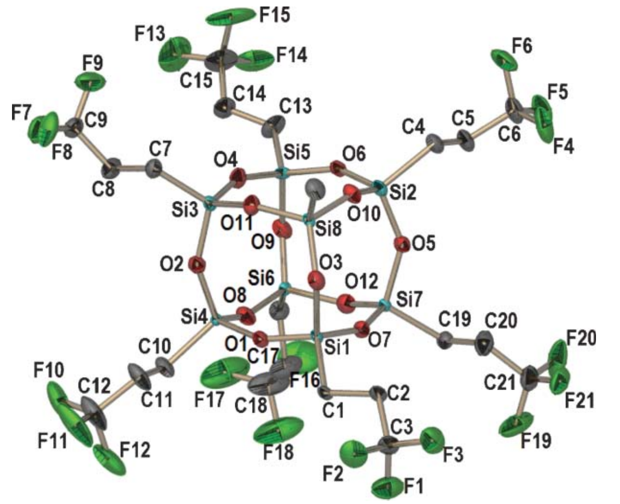


Fig. 2 ORTEP representation of **8** at 193 K with displacement ellipsoids shown at 30% probability. Hydrogen atoms are omitted for clarity.

highly disordered, and only one component of this disorder is shown in Fig. 2.

The hydrophobicity and oleophobicity of the F-POSS solids were tested using static water drop shape analysis. The relationship between contact angle and surface energy is governed by Young's equation, and relates the interfacial tensions of the surface of a liquid to its liquid and gas phases.[20] Contact angle measurements were performed on F-POSS coatings prepared from hexafluorobenzene solutions that were spin cast onto glass (Fig. 3). The application of water to these solids showed non-wetting behavior, with contact angles greater than 90°. Therefore, these solids are considered hydrophobic and, to some extent, oleophobic. Water drops did not adhere to the POSS coatings and subsequently rolled off as the surface was tilted beyond 90°.

The well-adhered, powder-like films possessed nanometer-scale surface roughness due to solvent evaporation during the spin coating process, as measured by atomic force microscopy (AFM) analysis. The surface roughness, in addition to low surface energy fluorine atoms on the POSS cages, contributes to the non-wetting behavior.[21] As an example, Fig. 4 shows the AFM-generated surface of **4**, with an average measured surface roughness of 20 nm. This surface morphology was consistent for all of the spin cast surfaces of F-POSS compounds **2–5**.

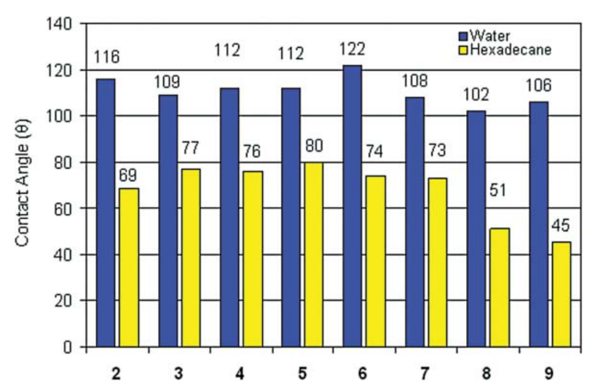


Fig. 3 Water and hexadecane contact angles measured on fluoroalkyl$_8$T$_8$ POSS (**2–9**) spin coated surfaces.

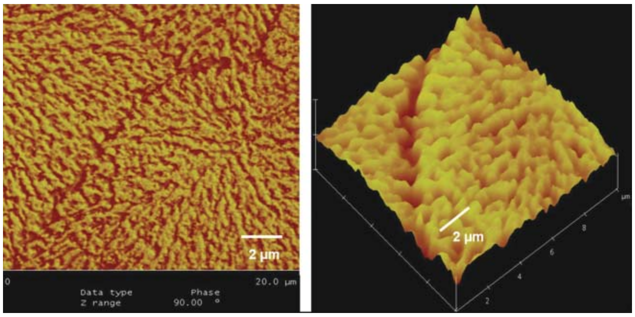


Fig. 4 AFM phase image of **4** (left) taken of a spin cast surface with nanometer-sized surface roughness (right).

Compared to the fluoro-substituted silsesquioxanes **2–7**, the alkyl **8** and aryl **9** corner-capped analogues showed approximately a 10% decrease in water contact angle. However, there was a significant decrease in the hexadecane repellency of 36%, on average, that can be attributed to increased miscibility between the hydrocarbon chain on POSS and the hydrocarbon nature of hexadecane. A branched structure, as shown for **6**, was observed to produce the highest degree of water and oil repellency. Furthermore, hydrophobicity was most likely lowered for **7** due to hydrogen bonding of the water drop with the ether functionality. This ether functionality induces wetting by water, but does not affect the oleophobicity.

In conclusion, we have prepared a new class of fluorinated POSS (F-POSS) materials possessing both a high degree of water and hexadecane repellency. By controlling the degree of fluorine present and the architecture of the corner cap (R_f) substitution, we have been able to tune the materials to exhibit desirable wetting and melting properties. We anticipate that these materials could be used as drop-in modifiers for composite blends to enhance mechanical and surface energy properties.

We gratefully acknowledge the Air Force Office of Scientific Research and the Air Force Research Laboratory, Propulsion Directorate for their generous financial support. We would like to thank Dr Fook Tham at UC Riverside for his assistance in resolving the disorder issues in the crystal structure of **2**. We also thank Ms Sherly Largo (EAFB) for microscopy and optical imaging support. S. T. I. acknowledges the Air Force Institute of Technology Civilian Institution Program (AFIT/CIGD) for sponsorship.

Notes and references

1 H. Liu, S. Zheng and K. Nie, *Macromolecules*, 2005, **38**, 5088; M. E. Wright, D. A. Schorzman, F. J. Feher and R.-Z. Jin, *Chem. Mater.*, 2003, **15**, 264; R. M. Laine and A. Sellinger, *Macromolecules*, 1996, **29**, 2327.
2 S. Xiao, M. Nguyen, X. Gong, Y. Cao, H. B. Wu, D. Moses and A. Heeger, *Adv. Funct. Mater.*, 2003, **13**, 25.
3 G. B. Hoflund, R. I. Gonzalez and S. H. Phillips, *J. Adhes. Sci. Technol.*, 2001, **15**, 1199; R. I. Gonzales, S. H. Phillips and G. B. Hoflund, *J. Spacecr. Rockets*, 2000, **37**, 463.
4 F. J. Feher and D. A. Newman, *J. Am. Chem. Soc.*, 1990, **112**, 1931.
5 G. Li, L. Wang, H. Ni and C. U. Pittman, Jr., *J. Inorg. Organomet. Polym.*, 2001, **11**, 123; J. F. Brown and L. H. Vogt, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 4313; D. W. Scott, *J. Am. Chem. Soc.*, 1946, **68**, 356.
6 K. Koh, S. Sugiyama, T. Morinaga, K. Ohno, Y. Tsujii, T. Fukuda, M. Yamahiro, T. Iijima, H. Oikawa, K. Watanabe and T. Miyashita, *Macromolecules*, 2005, **38**, 1264; J. R. Hottle, J. Deng, H.-J. Kim, C. E. Farmer-Creely, B. D. Viers and A. R. Esker, *Langmuir*, 2005, **21**, 2250.
7 L. Zheng, S. Hong, G. Cardoen, E. Burgaz, S. P. Gido and E. B. Coughlin, *Macromolecules*, 2004, **37**, 8606; B.-Y. Kim and P. T. Mather, *Macromolecules*, 2002, **35**, 8378.
8 F. J. Feher, S. H. Phillips and J. W. Ziller, *J. Am. Chem. Soc.*, 1997, **119**, 3397; F. J. Feher, D. Soulivong and G. T. Lewis, *J. Am. Chem. Soc.*, 1997, **119**, 11323.
9 T. Sun, L. Feng, X. Gao and L. Jian, *Acc. Chem. Res.*, 2005, **38**, 644.
10 M. Sun, C. Luo, L. Xu, H. Ji, Q. Ouyang, D. Yu and Y. Chen, *Langmuir*, 2005, **21**, 8978; L. Zhai, F. C. Cebeci, R. E. Cohen and M. F. Rubner, *Nano Lett.*, 2004, **4**, 1349.
11 C. Neinhuis and W. Barthlott, *Ann. Bot.*, 1997, **79**, 677; W. Barthlott and C. Nenhuis, *Planta*, 1997, **202**, 1.
12 X. Gao and L. Jiang, *Nature*, 2004, **432**, 36.
13 L. Zhai, F. C. Cebeci, R. E. Cohen and M. F. Rubner, *Nano Lett.*, 2004, **4**, 1349; G. Crevoisier, P. Fabre, J.-M. Corpart and L. Leibler, *Science*, 1999, **285**, 1246.
14 K. K. S. Lau, J. Bico, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, G. H. McKinley and K. K. Gleason, *Nano Lett.*, 2003, **3**, 1701; T. Nishino, M. Meguro, K. Nakamae, M. Matsushita and Y. Ueda, *Langmuir*, 1999, **15**, 4321.
15 H. Yabu and M. Shimomura, *Chem. Mater.*, 2005, **17**, 5231; N. Takeshita, L. A. Paradis, D. Oner, T. J. McCarthy and W. Chen, *Langmuir*, 2004, **20**, 8131; T. J. McCarthy and D. Oner, *Langmuir*, 2000, **16**, 7777.
16 B. Qian and Z. Shen, *Langmuir*, 2005, **21**, 9007; Y. H. Erbil, L. A. Demirel, Y. Avci and O. Mert, *Science*, 2003, **299**, 1377.
17 F. Feher, *J. Am. Chem. Soc.*, 1986, **108**, 3850; F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741.
18 V. I. Lavrent'ev, *Russ. J. Gen. Chem.*, 2004, **74**, 1188; V. I. Laverent'ev and V. B. Durasov, *Zh. Obshch. Khim.*, 1992, **62**, 2722.
19 Crystallographic data for **2** and **8** have been submitted to the Cambridge Crystallographic Data Center (CCDC) with publication numbers 629369 and 642077, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712976a.
20 T. Young, *Philos. Trans. R. Soc. London*, 1805, **95**, 65.
21 A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546; R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.